Downloaded from rspa.royalsocietypublishing.org

PROCEEDINGS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

The Firing of Gaseous Mixtures by Compression

Lawrence Bradshaw

Proc. R. Soc. Lond. A 1907 **79**, 236-241
doi: 10.1098/rspa.1907.0036

Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click **here**

To subscribe to *Proc. R. Soc. Lond. A* go to: **http://rspa.royalsocietypublishing.org/subscriptions**

This journal is © 1907 The Royal Society

Downloaded from rspa.royalsocietypublishing.org

The Firing of Gaseous Mixtures by Compression.

By Lawrence Bradshaw, M.Sc., Ph.D.

(Communicated by Professor H. B. Dixon, F.R.S. Received January 28,—Read January 31, 1907.)

[Plate 3.]

During the course of the experiments described in the preceding paper, in which the movements of the flame in the explosion of electrolytic gas were recorded on a rapidly moving photographic film, we observed a new phenomenon. In addition to the ordinary effects accompanying the explosion,* the photograph showed a new luminous wave advancing from one end of the explosion-tube to meet the flame spreading slowly from the point of origin in the middle of the tube.

As we had not noticed this before in any one of the hundreds of photographs of the explosion-flame taken in this laboratory, we were led to suspect that this spontaneous ignition was caused by the peculiar shape of explosion-tube used for the first time in the above experiments. The electrolytic gas was enclosed in a glass tube, one end of which had been previously drawn out to a fine capillary in the blow-pipe flame, in order to facilitate the sealing of the tube after the gaseous mixture had been introduced. Following the device of H. B. Baker,† the capillary was first closed by allowing a small quantity of molten fusible metal to solidify in it. The end of the narrow tube could then be sealed off with a small flame without fear of the gases being prematurely exploded. One end of the tube was therefore shaped like a funnel (fig. 1, *a*).

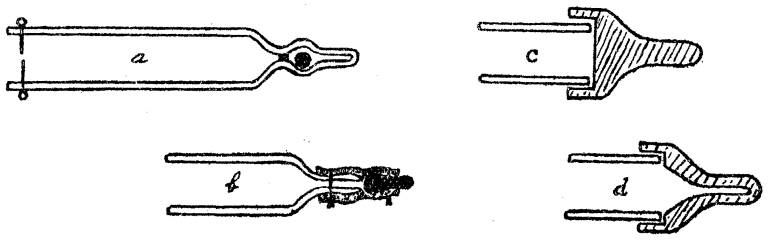

Fig. 1.

The wave in question seemed to originate at this end of the tube. We concluded that the gaseous mixture had fired spontaneously in this region, owing possibly to an invisible compression-wave compressing the gases in the

* H. B. Dixon, "The Movements of the Flame in the Explosion of Gases," 'Phil. Trans.,' vol. 200, p. 315, 1902.

† H. B. Baker, 'Chem. Soc. Journ.,' vol. 81, p. 400, 1902.

The Royal Society is collaborating with JSTOR to digitize, preserve, and extend access to *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character.* www.jstor.org

Downloaded from rspa.royalsocietypublishing.org

funnel to such an extent as to fire the mixture by the heat of compression. In the photographs the exact starting point of the flame cannot be seen; it is obscured by the clamp which held the tube in position.

At the suggestion of Professor H. B. Dixon, I therefore undertook the following research in order to obtain more evidence concerning the origin of the new combustion-wave, and the conditions under which it is set up.

In the experiments described in this paper no fusible metal was used; the capillary was sealed in the blow-pipe flame and the electrolytic gas introduced afterwards from the other end by evacuating the tube and filling it with the gas, the operation being repeated several times to get rid of all the air.

The photographs were taken in the usual way, viz., on a sensitised film stretched round a drum rotating with great rapidity, the film moving vertically downwards on the side nearest the explosion-tube, while the flame travelled in the tube horizontally. Only that portion of the tube between the firing wires and capillary end is shown in the photographs. The broad black band is caused by the clamp; the fine lines are due to narrow strips of paper pasted on the tube at intervals of three inches on each side of the firing-wires, and serve as reference lines. Fig. 2 will make the general arrangement of the tube clear. The spark was passed immediately to the right of the clamp holding the tube, at a distance of $7\frac{1}{2}$ inches from the conical end.

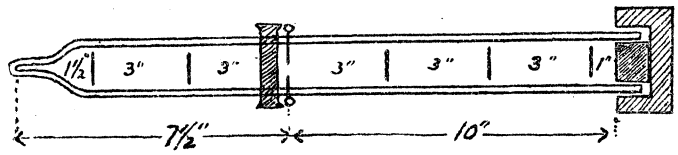

FIG. 2.

Fig. A (Plate 3) shows the movements of the flame in the explosion of $2H_2 + O_2$ in this tube. In the negative the spark may be detected a little to the right of the dark band; the flame spreads with increasing velocity to the right and to the left. When the flame has reached a point midway between the first and second reference lines to the left, *i.e.*, about $4\frac{1}{2}$ inches from the spark, a second flame* appears at the capillary end of the tube and moves forward with a velocity somewhat less than that of the flame initiated by the spark, and in the opposite direction. The two flames meet a little to the right of the first reference

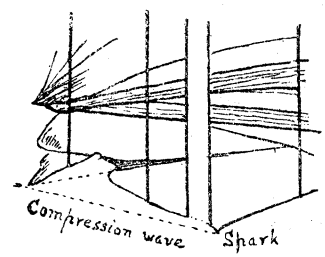

FIG. 3.

* This flame starts about 1/2700 sec. after the passage of the spark.

Downloaded from rspa.royalsocietypublishing.org

mark in the photograph. Fig. 3 is a plan showing, in outline, the movements of the flames.

It will be noticed that the initial flame is checked by a sound wave *reflected* from near the end of the tube.

The phenomenon is more clearly seen in fig. B (Plate 3), a photograph of the intensely bright flame in a mixture of carbon disulphide and oxygen (in the proportion $2CS_2 + 3O_2$) under the same conditions, the only difference being that in this case the spark-gap was 13 inches from the end of the tube; the film moved a little faster than in the previous case.

The same effects were observed in a large number of photographs, which it will not be necessary to reproduce here.

Experiments were made in which the relative diameters of the tube and capillary, and the length of the capillary, were varied, but the result was always the same, viz., the gas always ignited in the narrow portion of the tube. In a second series of experiments the distance between the spark gap and the capillary end of the tube was varied between 3 and 13 inches without affecting the result.

In all these experiments the end of the capillary was closed by sealing in the blow-pipe flame before introducing the explosive mixture.

It was next found that if this end is closed by means of a piece of stout pressure-tubing (wired on) and a piece of glass rod pressed against the orifice (fig. 1, *b*), no firing takes place. In this case the explosion was accompanied by a sharp click, as though the rubber tubing had yielded for an instant to the sudden pressure and then returned to its original position. The tube remained intact after the explosion. In one experiment, in which the glass stopper was pressed very tightly against the opening, the explosion was noiseless, and the gas was ignited in the capillary in just the same way as when this was hermetically sealed. Hence it appears that the new wave can only be set up when the end of the tube is quite rigid. This in itself is strong evidence in favour of the assumption that the gas is fired by compression.

It might be supposed that if an unyielding surface is all that is necessary to ensure spontaneous ignition, the same result could be brought about in a tube of uniform diameter closed with a flat metal plate. Fig. 1, *c*, shows a portion of such a tube. A tightly fitting brass cap was cemented on to the end and held in position by means of a clamp. This withstood the shock of the explosion, but the photograph shows no indication of any firing of the gases by compression, the picture obtained being similar in every respect to those usually obtained in tubes closed with rubber stoppers.

The brass end-piece was next removed from the tube, drilled to the shape shown in fig. 1, *d*, and then replaced on the original tube. This time the wave

Downloaded from rspa.royalsocietypublishing.org

was set up in the same manner as when the explosion tube had been drawn out to the same shape in the blow-pipe flame.

It follows that two of the conditions essential to the setting up of the wave are that the end of the tube must be funnel-shaped and unyielding. The wave produced is analogous to the tidal "bore" in a funnel-shaped estuary.

The distance from the firing-wires to the end of the tube is also important; it must be less than that required for the development of the detonation-wave in the gaseous mixture.

I have calculated the velocity with which a wave would have to travel from its point of origin in order to reach the end of the tube at the instant at which the gas ignites, as judged from the photographs.

The interval of time which elapses between the passage of the spark and the spontaneous inflammation of the gas at a point several inches distant from the firing-wires can be ascertained, when the velocity of the rotating film is known, by measuring on the film the vertical distance between the image of the spark and the image of the flame where it first appears. The amount of displacement is proportional to the time. In these experiments the film moved at the uniform rate of 19·84 metres per second, so that each centimetre, measured vertically, corresponds to about 1/2000 second.

A record was kept of the dimensions of the tubes, but the length from the spark-gap to the end of the tube can easily be estimated from the photographs by remembering that the strips of paper on the tube are 3 inches (7·62 cm.) apart, and the reference marks given by these in the photograph exactly 1 cm.

The rate of propagation of the wave is calculated from the length of the tube and the time taken by the wave to traverse it. I have made the various measurements as carefully as possible, but dealing as we are with velocities of the order of hundreds of metres per second over distances of a few centimetres, it is hardly to be expected that the results obtained in this way will be very concordant. Five of the best photographs of the explosion of $2H_2+O_2$ were selected and the following data obtained:—

Experiment No.	Distance from spark to end of tube.	Vertical displacement.	Velocity of film in metres per second.	Calculated velocity of compression-wave in metres per second.
	mm.	mm.		
C 1	229	8·5	19·84	533·6
C 3	137	5·5	19·84	494·9
C 14	221	7·0	19·84	604·8
C 16	196	7·2	19·84	539·5
CC 17	111	4·7	19·84	466·5
				Mean 527·9

Downloaded from rspa.royalsocietypublishing.org

The mean value for the velocity of the compression-wave was thus found to be 527·9 metres per second.

This approximates closely to the velocity which a sound-wave would have in electrolytic gas under the same conditions, calculated from Laplace's formula, $v = (P\gamma/\rho)^{\frac{1}{2}}$; ρ is the density of the gaseous mixture, and γ the ratio of the specific heat at constant pressure and at constant volume. Substituting in the above equation P = 1 atm. (1013300 dyne/cm.^{2}), $\rho = 0{\cdot}0005364$, and $\gamma = 1{\cdot}41$, we find $v = 522{\cdot}1$ metres per second.

Owing to the difficulty of obtaining a trustworthy value of γ for the mixtures of CS_2 with oxygen, the same method of examination cannot be employed. Such mixtures are, however, very valuable for studying the movements of the flame on account of the highly actinic nature of the light produced by them in exploding.

Although the rate calculated for the velocity of the wave which causes the ignition in the case of electrolytic gas agrees fairly well with that of sound in the same gas, it is difficult to believe that the firing is brought about by a sound-wave or series of sound-waves of the ordinary type, when the large amount of energy required to fire the mixture by the heat of compression is considered.

For the temperature of ignition of a mixture of hydrogen and oxygen in the proportion $2H_2 + O_2$, widely different values have been obtained by various observers.* Let us take, for the purpose of calculation, the lowest of these, viz., 555° C., given by Mallard and Le Chatelier.† The pressure which is necessary to produce this elevation of temperature, if the heating takes place adiabatically, may be calculated from the formula $T'/T = (p'/p)^{\gamma-1}$, where T, T′, are the absolute temperatures corresponding with the pressures p and p' respectively, and γ is, as before, the ratio of the specific heats at constant pressure and at constant volume. In the above experiments, T = 286° C., $p = 1$ atmosphere, $\gamma = 1{\cdot}41$, and it is found that the least pressure which will suffice to ignite the mixture is 13½ atmospheres.

Whatever the nature of the wave under discussion, it may be overtaken and destroyed by a detonation-wave when the latter is allowed to have a sufficient run. This is shown by the following experiment. A leaden pipe about 4 feet long was attached to a glass tube used in one of the earlier experiments, at the end furthest from the capillary. When the mixture is fired by a spark at the extreme end of this pipe, the wave of chemical combustion, slower at the start than the physical wave which precedes it, constantly increases its rate of propagation until it assumes the enormous

* See J. W. Mellor's 'Chemical Statics,' p. 447.

† 'Recherches sur la Combustion des Mélanges Explosifs,' Paris, 1883, p. 88.

Downloaded from rspa.royalsocietypublishing.org

velocity of the true detonation-wave. The detonation gains rapidly on the compression-wave and ultimately catches it up and absorbs it. The photograph shows that, under these circumstances, the gas is not fired in the capillary before the detonation-wave reaches it.

As far as the evidence goes, it seems to support the view that the spontaneous inflammation of a gas, under the conditions described in this paper, is caused by a wave of compression moving with about the same velocity as that of a sound-wave.

The foregoing experiments were carried out in the Frankland Laboratory of the Manchester University. I take this opportunity of expressing my thanks to Professor Dixon for the many valuable suggestions received from him, and for the interest he has taken in the work.

PROCEEDINGS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

PROCEEDINGS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES